Received: 16 March 2020 | Revised: 29 April 2020 | Accepted: 29 April 2020

DOI: 10.1002/rcm.8821

Rapid Communications in Mass Spectrometry WILEY

RESEARCH ARTICLE

Optimized switch-over between CHNS abundance and CNS isotope ratio analyses by elemental analyzer-isotope ratio mass spectrometry: Application to six geological reference materials

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Peer Review
The peer review history for this article is available at https://publons.com/publon/10.1002/rcm.8821

Rationale: Elemental abundances and isotopic ratios of carbon, nitrogen, sulfur and hydrogen have become important tools for reconstructing the evolution of Earth and life over geologic timescales, requiring accurate and precise analytical methods with high sample throughput. However, these measurements may require separate instruments for each task, such as an elemental analyzer (EA) with a thermal conductivity detector (TCD) for elemental abundances and an EA interfaced with a mass spectrometer for isotopic ratios.

Methods: To improve sample throughput and laboratory up-time, we developed a switch that allows converting an EA IsoLink™ system from a standalone mode using only a TCD to a mode for isotope ratio mass spectrometry (IRMS) within minutes. This permits accurate measurements of elemental abundances and isotopic ratios with high throughput and lower cost. We validated this method with six shale standards from the US Geological Survey (USGS) and compared our abundance data with those from another laboratory.

Results: Our results show that (a) abundance data agree well between the different laboratories and setups; (b) reproducible isotopic data can be obtained before and after the switch-over from EA standalone mode; and (c) the USGS rock standards cover a wide range in CHNS abundances and CNS isotopes, making them ideal reference materials for future geochemical studies.

Conclusions: This ideal analytical setup has the advantage that abundance measurements can be performed to determine optimal sample amounts for later isotopic analyses, ensuring higher data quality. Our setup eliminates the need for a separate EA while freeing up the mass spectrometer for other tasks during abundance measurements.

1 | INTRODUCTION

Carbon, nitrogen, hydrogen and sulfur – some of the major ingredients of life on Earth – have become important tools in Earth Sciences for reconstructing past environmental conditions. For example, total organic carbon (TOC) abundances in sedimentary rocks can provide information about biological productivity,[1] while organic carbon to sulfur ratios are sensitive to the redox state and salinity of

the water column under which those sediments were once deposited.[2–4] The carbon to hydrogen ratio in ancient biomass has become an important proxy for assessing the thermal maturity of organic matter,[5] and nitrogen abundances in phyllosilicates may serve as indirect evidence of past life.[6] Measurements of elemental abundances are also needed in preparation for precise isotopic analyses where the amount of analyte needed exceeds the blank while staying below the saturation limit of the mass spectrometer.

The stable isotope ratios of sulfur ($^{34}S/^{32}S$) in sedimentary and igneous rocks are widely used as redox indicators.[7–9] Organic carbon isotopic ratios ($^{13}C/^{12}C$) in ancient biomass track biological metabolisms and have been used to date the antiquity of life on Earth.[10,11] Nitrogen isotope ratios ($^{15}N/^{14}N$) in sedimentary rocks are sensitive to the redox state of the upper column and can be used to reconstruct the evolution of biological nitrogen metabolisms.[12–14] The isotope ratios of carbon, nitrogen and sulfur are commonly measured by gas source isotope ratio mass spectrometry (IRMS). For sedimentary rocks, CO_2, N_2 and SO_2 gases are generated by flash combustion in an elemental analyzer (EA) that is interfaced with an isotope ratio mass spectrometer. This EA-IRMS method can also provide information about total C, N and S elemental abundances in a sample if the peak areas are calibrated with standards of known elemental composition. However, this approach has the disadvantage that it cannot provide H abundances, because H_2O vapour is trapped with a desiccant to optimise ionisation of the other gases in the mass spectrometer. Secondly, for samples where abundances are unknown, the EA-IRMS method may require multiple analyses until accurate isotope ratios are obtained, because the peak size of each sample for each measured element needs to be close to that of the reference material and within the limits of the Faraday cup detectors. Some laboratories therefore use a second EA with a thermal conductivity detector (TCD) to measure elemental abundances separately from isotope ratios. The TCD has a wider operating range, i.e. it can provide accurate data for a wide range of masses (*e.g.*, Table 1), which is ideal for unknown materials. Where only one EA is available, however, the instrument may need to undergo complex reconfigurations to reliably alternate between stand-alone mode for elemental abundance measurements and IRMS mode for isotope ratio measurements. This is partly because EA-IRMS generally requires sharp peaks and excellent chromatography peak resolution, which can be achieved by ramping up the temperature of the gas chromatography (GC) column during sample analysis.[15] This temperature ramping of the GC column improves the elution of CO_2 and SO_2 while maintaining adequate separation between N_2 and CO_2 (e.g.,[15]). However, changing the temperature perturbs the baseline of the TCD, because it alters gas flow rates, meaning that the TCD cannot be used simultaneously with IRMS-mode. A reconfiguration or a separate EA would be needed.

To overcome the need for a separate EA and to avoid cumbersome system reconfiguration between methods for elemental abundance and isotope ratio measurements, this study developed an improved approach by implementing a switch for our EA-IRMS system. This switch allows alternating between stand-alone mode and IRMS mode within minutes. This tool allows us to obtain precise abundance measurements for all four elements (CHNS), which in turn helps optimise the mass of samples for subsequent isotope ratio analyses. Furthermore, the switch frees up the isotope ratio mass spectrometer for other applications while the EA is being used in stand-alone mode. At present, the switch is optimised for the EA IsoLink™ (Thermo Fisher Scientific, Bremen, Germany), which often possesses two GC ovens, if it is set up for sulfur isotopes. In this case, one of the two GC ovens has a temperature ramping function where the temperature can be raised during a sample analysis, allowing adequate separation of N_2, CO_2 and SO_2, paired with optimal peak shapes.[15] However, the switch would be adaptable for laboratories that possess a different EA with a single GC column that requires different operating conditions for IRMS and standalone modes. In that case, an isothermal GC oven could be constructed relatively easily and added to the EA setup together with the switch.

In this study, we tested this method with six international reference materials of shale powders from the US Geological Survey. These shales show a wide range in elemental and isotopic compositions. It is the hope of the authors that these standards will

TABLE 1 List of geological reference materials from the US Geological Survey (USGS, Reston, VA, USA)

Identifier	Lot #	Geological unit	Age	Mass range IRMS St Andrews [mg]			Mass range EA stand-alone St Andrews [mg]	Mass range EA stand-alone Milan [mg]
				$^{13}C/^{12}C$	$^{34}S/^{32}S$	$^{15}N/^{14}N$		
SBC-1*	594	Bush Creek shale	Pennsylvanian	2–3	2–3	19–21	5–15	15–25
SCo-1	30	Cody shale	Late cretaceous	9–12	30–35	30–35	5–50	15–20
SDo-1	719	Devonian Ohio shale, Huron Mbr	Devonian	0.2–0.5	0.2–0.5	9–10	1–10	7–10
SGR-1	536	Green River shale, mahogany zone	Eocene	0.5–0.7	2–3	2–3	1–25	3–4.5
ShBOQ-1*	1,735	Boquillas shale	Late cretaceous	1–2	2–3	20–25	3–14	7–8
ShWFD-1*	535	Woodford shale	Devonian-Mississippian	1–2	1–2	5–8	2–24	7–10

*SBC-1, ShBOQ-1 and ShWFD-1 were provided by Dr Stephen Wilson, USGS.

become more widely used as quality control standards in gas source geochemistry laboratories, where such standards are currently not well established.

2 | METHODS

The switch device was installed on a Thermo Fisher Scientific™ EA Isolink™ IRMS system (THermo Fisher Scientific, Bremen, Germany) that is configured for the determination of carbon, nitrogen and sulfur stable isotope ratios in the St Andrews Isotope Geochemistry (StAIG) laboratories at the University of St Andrews, UK. The EA IsoLink is interfaced with a Thermo Fisher Scientific™ MAT 253™ isotope ratio mass spectrometer via a Thermo Fisher Scientific™ ConFlo IV Universal Interface. The elemental abundance data obtained from the EA IsoLink, when operated in stand-alone mode, were cross-checked with elemental abundance measurements performed with the same type of EA at the Thermo Fisher Scientific laboratory in Rodano, Milan, Italy.

2.1 | Materials used in St Andrews

The EA in the St Andrews setup was equipped with a zero-blank 50-slot autosampler (Costech, Milan, Italy). The samples were combusted in a standard quartz reactor column (QZ1269.001 from Elemtex, Callington, UK) packed with tungstic oxide (part No. OX1352.100 from Elemtex) and electrolytic copper (part No. B1239 from Elemental Microanalysis, Okehampton, UK). Once installed into the EA, this reactor was gradually conditioned until it reached an operating temperature of 1,020°C. The water trap, which was kept at room temperature, was filled with magnesium perchlorate (part No. B1275 from Elemental Microanalysis). The samples were weighed into 8 x 5 mm tin capsules (part No. 24006400 from Thermo Fisher Scientific). In EA stand-alone mode, 8–10 mg of vanadium pentoxide (V_2O_5, part No. B4001 from Elemental Microanalysis) was added to each capsule for improved sulfur conversion. Without V_2O_5 in stand-alone mode, we sometimes observed double-peaks for SO_2, probably because the sample quantities are relatively large and may not combust well with O_2 alone. We did not add V_2O_5 for analyses in IRMS mode, where sample quantities were significantly smaller. We note that previous studies have added V_2O_5 for isotopic analyses,[16–18] but at least in the case of the SGR-1 reference material it was not found to have a significant effect.[16] Some studies have also documented traces of N contamination with very high $^{15}N/^{14}N$ ratios in certain brands of V_2O_5, which requires additional data correction and introduces uncertainties to the results.[17,18] We therefore avoided V_2O_5 in this study, but more work on the importance and purity of V_2O_5 may be beneficial for the isotope community.

In stand-alone mode, the abundances of C, H, N and S were calibrated with a sulfanilamide standard (Part No. B2048 from Elemental Microanalysis), using the K-factor method, where a linear fit between analyte quantity and measured peak area is calculated from a single standard. For EA-IRMS measurements, isotopic ratios were calibrated by two-point calibration, using the glutamic acids USGS-41 and USGS-40 (USGS) for carbon and nitrogen and the silver sulfides IAEA-S2 and IAEA-S3 (International Atomic Energy Agency, Vienna, Austria) for sulfur. Glutamic acids and silver sulfides were mixed within one capsule to be able to calibrate for all three isotopic systems within one run. No negative effects on isotopic reproducibility were noticed to result from this mixing. For quality control, we used USGS-62 (caffeine) and IAEA-S1 (silver sulfide), which returned values within 0.2‰, 0.2‰ and 0.5‰ of the expected values for carbon, nitrogen and sulfur isotope ratios, respectively. Isotopic ratios are expressed in standard delta notation ($\delta = [R_{sample}/R_{standard} - 1]$), where $R = {}^{13}C/{}^{12}C$ for carbon, $^{15}N/^{14}N$ for nitrogen and $^{34}S/^{32}S$ for sulfur. The reference standards are atmospheric air N_2, V-PDB and V-CDT, respectively. The elemental abundances calculated from sample analysis in IRMS mode were calibrated with a series of USGS-41 and IAEA-S1 standards at different masses (0.05–0.3 mg and 0.05–0.2 mg, respectively) to create a linear regression between analyte amount and peak area.

The shale samples that we analyzed are listed in Table 1. SGR-1 and SCo-1 are currently available for purchase from the US Geological Survey. SDo-1 has been phased out, but aliquots of it are still available in many laboratories. ShBOQ-1, ShWFD-1 and SBC-1 are new reference materials that are currently under development by the USGS and will soon be available for purchase. SDo-1 and SGR-1 have previously been proposed as international isotopic reference materials for organic carbon and nitrogen,[19] but they have to our knowledge so far not been systematically tested for sulfur. In addition, the H abundances on these materials have not yet been published. For the bulk of this study, we chose to analyze these materials without any chemical pre-treatment such as decarbonation, because such treatments may introduce variability between laboratories[20,21] and hamper the utility of these standards for quality control. However, we will also present organic carbon isotope data obtained after decarbonation with hydrochloric acid. For this treatment, 0.5 g of powder were weighed into a pre-combusted (500°C for 4 hours) Pyrex glass tube and mixed with 10 mL of 2 M HCl (reagent grade, diluted with 18.2 MΩ deionised water). The samples were loosely capped and left to react overnight in a sealed acid-proof oven at 70°C. They were then centrifuged, and the acid was decanted. The decarbonated powders were washed three times with deionised water and then left to dry for three days in the oven at 70°C.

2.2 | Analytical setup in St Andrews

The EA IsoLink at St Andrews contains both a ramped GC oven for isotopic analyses and a second isothermal GC oven, which is used for elemental abundance measurements.[15] To facilitate rapid switching between methods, it is critical that both GC columns are kept under helium to avoid intake of air and moisture, which would require lengthy bake-out routines and thus longer switching times between the methods. To achieve this, we installed an additional helium

pressure regulator (part No. 1258810 from Thermo Fisher Scientific) and an 8-port/2-position manual Valco valve with 1/16″ fittings (part No. C8UWE from VICI, via Restek, Saunderton, UK) (Figure 1A). Both parts were placed immediately next to the EA, on the right-hand side, to minimize the total length of the gas flow path. The regulator was used to set the auxiliary helium flow through the GC column that is unused at any given time. This was the isothermal gas chromatograph in IRMS mode and the ramped gas chromatograph in stand-alone mode (Figure 1). The pressure was set to 0.5 bar, yielding a constant He flow rate of 8 mL/min. All helium used in our setup was CP grade (99.999%, from BOC, Aberdeen, UK). The 8-port Valco valve allows the flow paths to be changed such that the auxiliary He from the new regulator goes either through the isothermal GC oven when the instrument is in IRMS mode (Figure 1A) or through the ramped GC oven when the instrument is in stand-alone mode (Figure 1B). The combustion reactor column was the same in both methods. The water trap can be removed for stand-alone applications, which allows for H-abundance measurements to be made sequentially with carbon, nitrogen and sulfur. All capillaries used in the sample gas flow pathway were 1/16″ sulfinert; other capillaries were made from stainless steel (Figure 1).

The method for the IRMS mode was documented previously.[15] However, briefly, in IRMS mode, the He flow rate through the reactor started at 180 mL/min and was reduced to 50 mL/min after 110 seconds. At this point, the V2 split valve in the helium management (HeM) system of the EA IsoLink was automatically closed. This feature improves elution of all gases from the reactor at high flow rate while optimizing the transfer of CO_2 and SO_2 across the GC column at a lower flow rate. The temperature of the ramped GC oven was initially set to 40°C and ramped to 240°C after 160 seconds to optimize elution of SO_2. The gases were then carried into the ConFlo IV through the HF1 inlet. The reference He flow, which supplies the TCD

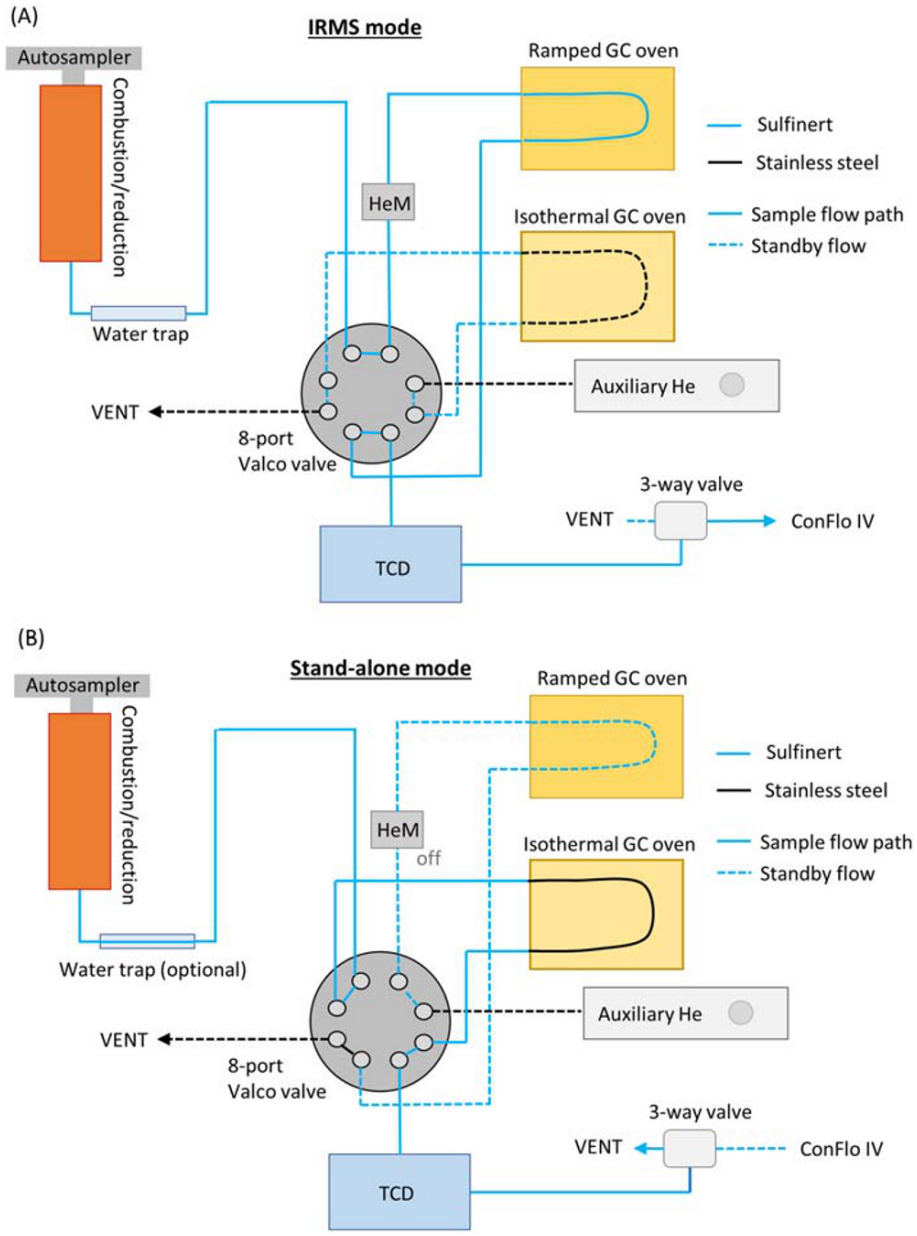

FIGURE 1 Schematic of the EA-IRMS setup with a switch-over Valco valve to alternate between EA-IRMS mode (A) and EA stand-alone mode (B) [Color figure can be viewed at wileyonlinelibrary.com]

and was therefore not used in this setup, was kept at a rate of 10 mL/min. Measurements were carried out with the Isodat Software Suite (Thermo Fisher Scientific).

In stand-alone mode, the He carrier flow rate was set to 140 mL/min and the reference flow rate was kept at 100 mL/min. The flow rates were held constant throughout the analytical run. After eluting from the GC column and passing through the TCD, the gases were vented into a hose of the laboratory's extraction system rather than introduced into the ConFlo IV. This is because the amount of material needed for stand-alone measurements is significantly larger than for isotope measurements, and it includes H_2O vapour, which should be kept out of the open split in the ConFlo IV; this ensures that there is no introduction of H_2O into the ion source. Furthermore, this setup frees up the mass spectrometer for other applications that can be introduced via the ConFlo IV through the HF2 or LF port, or via the Dual Inlet. While in stand-alone mode, the EA was controlled using the Eager*Smart* Data Handling Software (Thermo Fisher Scientific). In both analytical modes described above, the O_2 gas injection to aid combustion in the reactor was introduced as a 5-second pulse with a flow rate of 250 mL/min.

2.3 | Methods and analytical setup in Milan

At Thermo Fisher Scientific in Rodano, Milan, we undertook additional elemental abundance measurements. The reactor column in the EA (Flash*Smart*™, Thermo Fisher Scientific) was packed with copper oxide wire and electrolytic copper (both supplied by Thermo Fisher Scientific), and held at a temperature of 950°C. All other parameters, including flow rates and GC oven temperature, were the same as in St Andrews, but rather than going through a Valco valve, the gas flow was directed immediately to the GC column (Figure 2). Abundances were calibrated with BBOT (2,5-bis(5-tert-butyl-2-benzo-oxazol-2-yl, p/n 33,835,210 from Thermo Fisher Scientific), using the K-factor method.

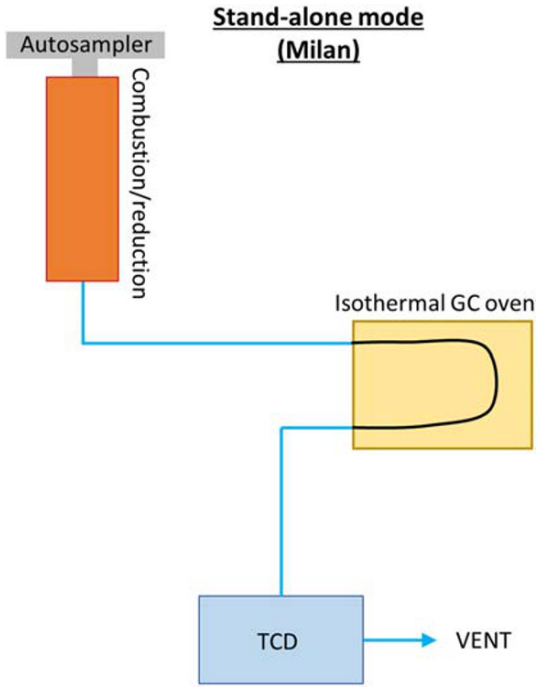

FIGURE 2 Schematic of the EA standalone setup in Milan [Color figure can be viewed at wileyonlinelibrary.com]

For organic carbon measurements, an aliquot of each sample was decarbonated with 6 M HCl within silver capsules.[20] The untreated powder was first weighed into the capsule and then treated with a few drops of acid. During this process, the capsules were placed on a hotplate at 65°C. This procedure was repeated about three times or until no more bubbling was observed, indicating complete decarbonation. The capsules were dried for one hour and then sealed for elemental analyses. A MAS Plus autosampler (Thermo Fisher Scientific, Rodano, Milan, Italy) was used to introduce the samples into the EA. This decarbonation technique, where the samples were weighed prior to acid addition, also provides an estimate of the total inorganic carbon content (TIC) as the difference between the total carbon and the total organic carbon. 8–10 mg of V_2O_5 were added to each capsule, except for the TOC measurements.

3 | RESULTS

The EA-IRMS data from St Andrews and elemental abundance data from both labs are shown in Tables 2 to 5.

3.1 | Isotopic data

For all three isotopic systems (C, S, N), the bulk rock data show a wide range (Figure 3): from −30.1‰ to −6.2‰ for $\delta^{13}C$ values, from −38.7‰ to +32.9‰ for $\delta^{34}S$ values, and from −2.9‰ to +17.8‰ for $\delta^{15}N$ values. The average standard deviations (1SD) are 0.36‰, 0.65‰ and 0.38‰, respectively. For $\delta^{13}C$ values, the largest uncertainties were found for ShBOQ-1 (1SD = 0.78‰), followed by SGR-1 (1SD = 0.47‰), which have the highest carbonate contents (Table 2). Both samples also display slightly larger errors for $\delta^{15}N$ values, of 0.82‰ and 0.35‰, respectively. For the decarbonated aliquots, which contain only organic carbon, the $\delta^{13}C_{org}$ values ranged from −30.5‰ to −24.0‰, and the average standard deviation was 0.16‰; ShBOQ-1 and SGR-1 are no longer anomalous in their standard deviations. It is likely that either carbonate is not as efficiently converted to CO_2 gas as organic carbon during whole rock analyses, or the ratio of organic carbon to inorganic carbon is heterogeneous within the samples. Both factors would lead to slightly larger uncertainties in bulk rock analyses.

For SDO-1 and SGR-1, our $\delta^{13}C_{org}$ data (−30.19 ± 0.18‰ and −29.51 ± 0.04‰) are in good agreement with published values of −30.0 ± 0.1‰ and −29.3 ± 0.1‰, respectively.[19] Also our bulk $\delta^{15}N$ data for SDO-1 and SGR-1 (−0.25 ± 0.31‰ and + 17.8 ± 0.35‰) agree well with those published from decarbonated aliquots reported by Dennen *et al* (−0.8 ± 0.3‰ and + 17.4 ± 0.4‰)[19] and in the case of

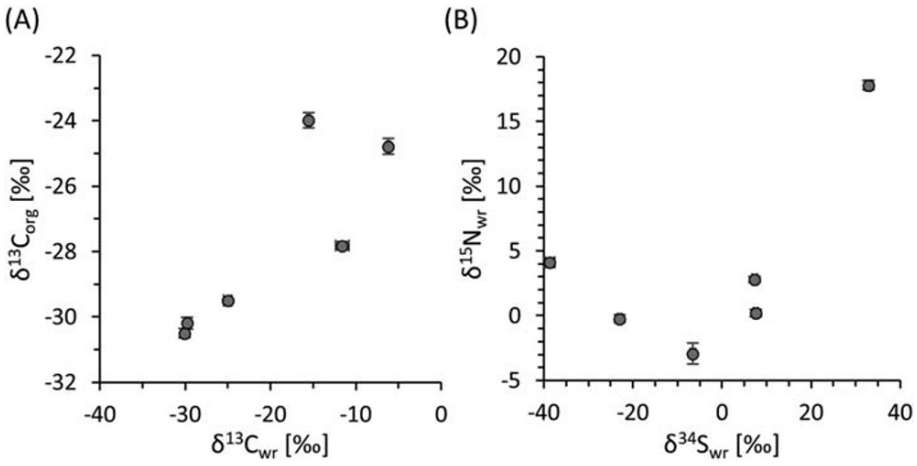

FIGURE 3 Isotopic data. (A) Organic carbon versus whole-rock (wr) carbon isotope ratios. (B) Whole-rock nitrogen versus whole-rock sulfur isotope ratios

$\delta^{15}N$ values for SGR-1 also with those by Han *et al* (+17.43 ± 0.17‰)[16] . We did not analyze the decarbonated powders for nitrogen and sulfur isotope ratios, because the effects of decarbonation were not the primary target of this study (but see[20,21]).

3.2 | Abundance data

Elemental abundances display a wide range over nearly 1–2 orders of magnitude for all four elements, and they show strong correlations between methods and laboratories (Figure 4 and 5). When using the EA stand-alone method in St Andrews, the relative error (1SD/mean) for total carbon is always better than 3%. For total sulfur, hydrogen and nitrogen, it is mostly better than 11%, except for SCo-1, which shows large uncertainties for all three elements. Overall, most of the data from St Andrews agree to within 10% or better with the results obtained in Milan. SCo-1 is again an outlier and the results for SBC-1 diverge for total hydrogen and nitrogen contents. Both SCo-1 and SBC-1 have comparatively large internal errors in our analyses at St Andrews (Table 2-4). The precision (RSD) is better in Milan than at St

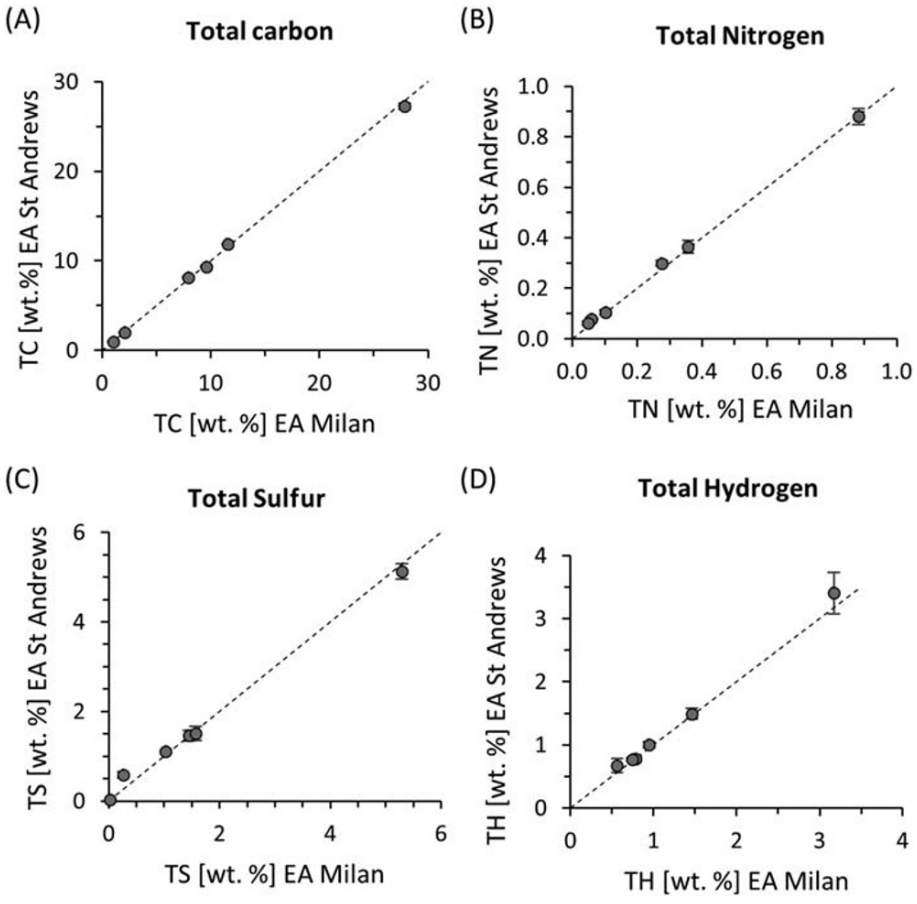

FIGURE 4 Total abundances from whole-rock samples for carbon (a), nitrogen (B), sulfur (C) and hydrogen (D). Comparing data between the elemental analyzer (EA) in stand-alone mode from laboratories in Milan and St Andrews. Dashed line = 1:1 line

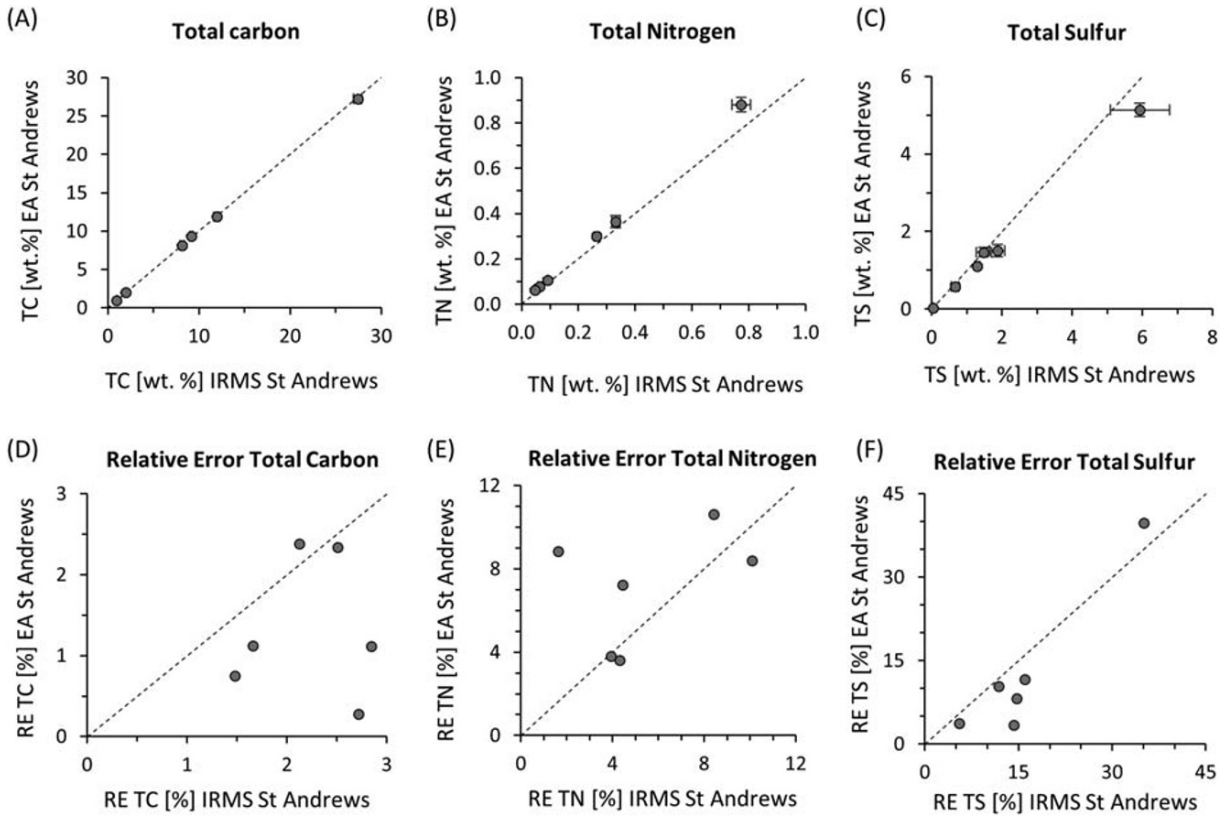

FIGURE 5 Total abundances and relative errors from whole-rock samples for carbon (a and D), nitrogen (B and E), and sulfur (C and F). Comparing data from the elemental analyzer (EA) in stand-alone mode with data obtained from the EA-IRMS system, both in St Andrews. Dashed line = 1:1 line

Andrews, which may be attributed to the fact that samples were analyzed in a random order in St Andrews rather than in groups of the same material as in Milan. Furthermore, the sample masses in Milan fell within a narrower range (Table 1). However, the precision obtained at St Andrews is acceptable for rock samples, demonstrating that the comparatively wide range of sample amounts that was used in St Andrews works sufficiently well.

When comparing our EA stand-alone data with abundances measured with the IRMS method (Figure 5), agreements for total carbon abundances are better than 2%, but for the EA-IRMS method the relative error for total carbon is slightly larger (2.2% on average) than for the stand-alone method (1.3%). In contrast, for nitrogen and sulfur, the two methods display larger offsets of 10% or more, for SCo-1 and SBC-1. The relative errors tend to be larger for the IRMS method than for the stand-alone method (Figures 5D-F).

For SGR-1 and SDo-1, for which organic carbon and nitrogen abundances have previously been assessed, our results are in good agreement with published values. For SGR-1, Dennen *et al*[19] measured a TOC content of 24.01 ± 0.38 wt. %, which agrees well with our TOC value of 24.56 ± 0.06 wt. % that we obtained in Milan. For TN, our abundances values of roughly 0.88 wt. % are higher than the value of 0.81 ± 0.02 wt. % from Dennen *et al*,[19] but close to the value of 0.91 wt. % from Han *et al*.[16] For SDo-1, both our TOC (9.33 ± 0.01 wt. % from Milan) and TN values (0.36 ± 0.03 wt. % from St Andrews and 0.36 ± 0.001 wt. % from Milan) agree well with published data, where TOC is 0.64 ± 0.19 wt. % and TN = 0.36 ± 0.01 wt. %.[19]

4 | DISCUSSION

4.1 | Method evaluation

The mechanical switch between the IRMS and stand-alone methods worked overall seamlessly. After switching, we allowed the previously unused GC column to purge at a higher He flow rate for several minutes. This time was also used to install or remove the water trap as needed. Analyses could be carried out with the same reactor column.

The data suggest that our EA-IRMS method generates good quality isotopic data, as evidenced by acceptable uncertainties and good reproducibility of published values for SDo-1 and SGR-1. The EA stand-alone method for elemental abundances appears to produce consistent data between laboratories, except for materials that have very low abundances in sulfur and perhaps nitrogen. In contrast, the EA-IRMS method, when calibrated for abundances, appears to be less consistent and internally slightly less reproducible. For some geochemical studies where differences in elemental abundances of a

TABLE 2 Carbon data from the EA-IRMS and EA stand-alone systems in St Andrews and Milan. TC = total carbon, wr = whole rock, org = organic carbon, DC = decarbonated, # = number of analyses, σ = standard deviation of preceding column, RE = relative error. Measurements were excluded if the peak area was less than 10 Vs in EA-IRMS mode, or if the detectors were saturated. Isotopic data are reported in per mille (‰); abundance data are in weight percent

	St Andrews IRMS								St Andrews EA stand-alone				Milan EA stand-alone								
ID	TC [wt. %]	σ	RE [%]	$\delta^{13}C_{wr}$ [‰]	σ	$\delta^{13}C_{org}$ [‰]	σ	#C	TC [wt. %]	σ	RE [%]	#wr	TC [%]	σ	RE [%]	TOC [wt. %]	σ	RE [%]	TIC [%]	#dc	#wr
SBC-1	1.966	0.042	2.1	−15.53	0.24	−23.98	0.23	12	1.982	0.047	2.4	9	2.080	0.018	0.8	1.110	0.005	0.4	0.970	5	9
SCo-1	0.971	0.024	2.5	−6.18	0.26	−24.78	0.25	16	0.961	0.023	2.3	11	1.060	0.011	1.0	0.283	0.003	1.1	0.777	5	10
SDO-1	9.164	0.136	1.5	−29.78	0.25	−30.19	0.18	13	9.347	0.070	0.8	9	9.620	0.031	0.3	9.330	0.009	0.1	0.290	5	10
SGR-1	27.405	0.455	1.7	−25.02	0.47	−29.51	0.04	23	27.254	0.306	1.1	15	27.840	0.103	0.4	24.560	0.061	0.3	3.280	5	10
ShBOQ-1	11.934	0.324	2.7	−11.60	0.78	−27.82	0.12	9	11.870	0.033	0.3	11	11.550	0.104	0.9	5.270	0.025	0.5	6.280	5	10
ShWFD-1	8.152	0.232	2.8	−30.10	0.15	−30.51	0.14	13	8.135	0.091	1.1	12	7.930	0.039	0.5	7.700	0.041	0.5	0.230	5	10

TABLE 3 **Sulfur data from the EA-IRMS and EA stand-alone systems in St Andrews and Milan.** TS = total sulfur, wr = whole rock. # = number of analyses, σ = standard deviation of preceding column, RE = relative error. Measurements were excluded if the peak area was less than 10 Vs in EA-IRMS mode, or if the detectors were saturated. Isotopic data are reported in per mille (‰); abundance data are in weight percent

	St Andrews IRMS						St Andrews EA stand-alone				Milan EA stand-alone			
ID	TS [wt. %]	σ	RE [%]	$\delta^{34}S_{wr}$[‰]	σ	#S	TS[wt. %]	σ	RE [%]	# wr	TS [wt. %]	σ	RE [%]	# wr
SBC-1	0.670	0.107	16.0	−38.71	1.06	14	0.583	0.068	11.6	9	0.259	0.002	0.8	9
SCo-1	0.045	0.016	35.0	7.33	0.61	14	0.023	0.009	39.7	11	0.025	0.000	0.8	10
SDO-1	5.931	0.841	14.2	−22.98	0.46	7	5.132	0.173	3.4	9	5.290	0.014	0.3	10
SGR-1	1.482	0.218	14.7	32.92	0.69	18	1.463	0.119	8.1	15	1.450	0.029	2.0	10
ShBOQ-1	1.869	0.220	11.8	−6.55	0.54	13	1.503	0.156	10.4	11	1.570	0.029	1.8	10
ShWFD-1	1.297	0.071	5.5	7.56	0.55	9	1.108	0.041	3.7	12	1.030	0.009	0.8	10

TABLE 4 **Nitrogen data from the EA-IRMS and EA stand-alone systems in St Andrews and Milan.** TN = total nitrogen, wr = whole rock, # = number of analyses. σ = standard deviation of preceding column, RE = relative error. Measurements were excluded if the peak area was less than 10 Vs in EA-IRMS mode, or if the detectors were saturated. Isotopic data are reported in per mille (‰); abundance data are in weight percent.

	St Andrews IRMS						St Andrews EA stand-alone				Milan EA stand-alone			
ID	TN [wt. %]	σ	RE [%]	$\delta^{15}N_{wr}$[‰]	σ	#N	TN [wt. %]	σ	RE [%]	# wr	TN [wt. %]	σ	RE [%]	# wr
SBC-1	0.064	0.006	10.1	4.12	0.32	5	0.079	0.007	8.4	9	0.058	0.000	0.7	9
SCo-1	0.047	0.004	8.4	2.79	0.21	8	0.062	0.007	10.6	11	0.049	0.001	1.2	10
SDO-1	0.331	0.015	4.4	−0.25	0.31	6	0.364	0.026	7.2	9	0.357	0.001	0.4	10
SGR-1	0.773	0.033	4.3	17.80	0.35	22	0.880	0.032	3.6	15	0.883	0.010	1.1	10
ShBOQ-1	0.092	0.002	1.6	−2.93	0.82	5	0.105	0.009	8.8	11	0.102	0.002	2.0	10
ShWFD-1	0.264	0.010	3.9	0.19	0.29	6	0.299	0.011	3.8	12	0.275	0.002	0.8	10

TABLE 5 **Hydrogen data from the EA stand-alone systems in St Andrews and Milan.** TH = total hydrogen, wr = whole rock, # = number of analyses, σ = standard deviation of preceding column, RE = relative error. Abundance data are in weight percent

	St Andrews EA stand-alone				Milan EA stand-alone			
ID	TH [wt. %]	σ	RE [%]	# wr	TH [wt. %]	σ	RE [%]	# wr
SBC–1	0.775	0.037	4.8	9	0.785	0.006	0.8	9
SCO–1	0.673	0.109	16.1	11	0.562	0.006	1.1	10
SDO–1	1.492	0.088	5.9	9	1.460	0.025	1.7	10
SGR–1	3.407	0.328	9.6	15	3.170	0.017	0.5	10
SHBOQ–1	0.766	0.028	3.7	11	0.747	0.011	1.5	10
SHWFD–1	1.005	0.048	4.8	12	0.944	0.010	1.0	10

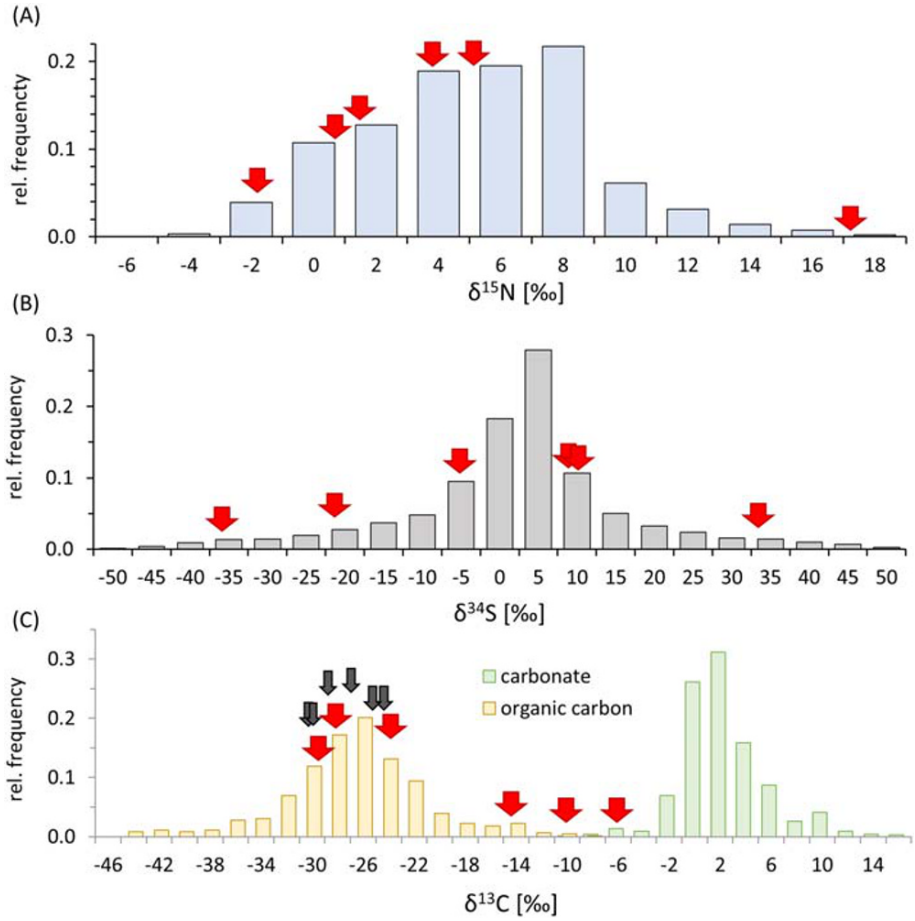

FIGURE 6 Comparison of the isotopic data from the USGS reference standards with compiled databases of sedimentary rocks. (A) Nitrogen isotope ratios in whole-rocks.[12] (B) sulfur isotope ratios in whole-rocks and sulfide separates.[22] (C) carbon isotope ratios from organic (yellow bars) and inorganic carbon (green bars).[23] Red arrows mark positions of whole-rock data from the USGS shales. Black arrows in panel c mark organic carbon data from the decarbonated shale aliquots [Color figure can be viewed at wileyonlinelibrary.com]

few tenths of a percent are not significant, the accuracy and precision provided by the EA-IRMS method are enough, but higher quality data can be obtained with the EA in stand-alone mode, using the TCD. This is especially true if samples are analysed in groups of the same material rather than in random order and with a narrower range of sample masses, as evidenced by the difference between the St Andrews and Milan data. This outcome is unsurprising, because the EA-IRMS system was first and foremost developed to measure isotopic ratios, and is consequently more sensitive, while the TCD inside the EA is optimised for abundance measurements.

4.2 | Reference materials

The six USGS shale standards cover a wide range in carbon, nitrogen and sulfur isotopic ratios that spans a large portion of the range archived in the sedimentary rock record for each of these isotopic systems (Figure 6). In addition, their elemental abundances are diverse. With some exceptions (Table 2), the isotopic reproducibility is good and the abundance reproducibility is adequate for materials with >0.1% nitrogen and > 0.5% sulfur. These shales may therefore provide useful reference materials in future studies of light stable isotopes and abundances in siliciclastic sedimentary rocks. We hope that they will become more widely used, such that a larger database can be compiled over time.

5 | CONCLUSIONS

We have developed a mechanical switch for our EA IsoLink that allows alternating between stand-alone abundance measurements with the built-in TCD and isotopic measurements with an isotope ratio mass spectrometer (Figure 1). This modification alleviates the need for a separate EA to carry out abundance measurements in preparation for isotopic analyses. Isotopic determinations typically require a narrow range of sample masses to obtain optimal peak sizes comparable with those of reference materials, and this mass range may differ markedly between carbon, nitrogen and sulfur isotopic measurements. For example, it is possible that an IRMS run optimized for sulfur does not produce a detectable peak for nitrogen, such that multiple runs are required to determine the optimal sample amount as well as the isotopic ratio for each element. Being able to perform abundance measurements with the EA in stand-alone mode, where larger sample amounts can be analysed without saturating the detector, alleviates this problem. Our modification keeps the entire system constantly under helium, but the flow rates are low, such that total helium consumption is not significantly increased. We have successfully tested the method with six USGS shale standards that show a wide range of isotopic and abundance values with mostly adequate reproducibility. We hope that after further analyses these materials will become established for inter-laboratory comparisons of analytical accuracy in future biogeochemical studies.

ACKNOWLEDGEMENTS

EES thanks Tommaso Di Rocco for technical assistance and acknowledges start-up funds from the School of Earth & Environmental Sciences, St Andrews. We thank Dr Stephen Wilson (USGS) for providing some of the reference materials.

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How to cite this article: Stüeken EE, M de Castro, Krotz L, Brodie C, Iammarino M, Giazzi G. Optimized switch-over between CHNS abundance and CNS isotope ratio analyses by elemental analyzer-isotope ratio mass spectrometry: Application to six geological reference materials. *Rapid Commun Mass Spectrom*. 2020;34:e8821. https://doi.org/10.1002/rcm.8821